3 Analysis of Variations in Particulate Matter

3.1 Day-of-Week Patterns of Particulate Matter and its Species at Selected Sites in California

3.1.1 Abstract

This chapter summarizes an analysis of variations, by day of week, in concentrations of particulate matter (PM) in California. Because volatile organic compounds (VOCs) and oxides of nitrogen (NO_X) and not only precursors of ozone but also of secondary PM, it is useful to know whether the variations by day of week in these precursors are also evident in PM data. Concentrations of PM $\leq$ 10 microns and $\leq$ 2.5 microns in aerodynamic diameter (PM10; PM2.5) were analyzed. Analysis of PM concentrations indicates a general weekly pattern with the maximum occurring late in the workweek and the minimum occurring on weekends (especially Sunday); however, the pattern is not statistically significant at all sites and areas.

Given the wide variety of sources contributing to PM (e.g., primary particles and secondary particles from combustion sources) and the factors listed above, interpretation of these results in terms of weekday/weekend emissions differences is complex and should be done with caution. Performing a comprehensive air quality data analysis and a three-dimensional modeling study that would test the impact of emissions changes associated with changes in emission levels, timing, spatial distributions, etc, would lead to a more accurate characterization of the weekday/weekend pattern of PM.

3.1.2 Introduction

Suspended particulate matter has been shown to affect public health when susceptible populations are exposed to excessive concentrations. Airborne PM is not a single pollutant, but rather it is a mixture of many subclasses of pollutants with each subclass containing many different chemical species. Particulate matter can exist in the liquid or solid phase and its size spans several orders of magnitude, from a molecular cluster of 0.005 μm in aerodynamic diameter to coarse particles on the order of 100 μm. These particles can be introduced directly into the atmosphere from natural activities (for example, sea spray and volcanic eruptions) or from anthropogenic pollution sources. As they evolve in the atmosphere, their chemical and physical properties **C** and hence their characteristics, such as light scattering and toxicity **C** change by accumulation of atmospheric gas-phase chemical reaction products or through heterogeneous reactions with gas-phase species.

Gaseous sulfur dioxide emitted from fossil fuel combustion, as well as organic species emitted from both anthropogenic and biogenic sources, can

react in the atmosphere to form particulate sulfates or secondary organic aerosols, respectively. Additionally, gas-phase emissions of nitrogen oxides from combustion sources undergo homogeneous atmospheric reactions to produce gaseous species including N_2O_5 and nitric acid. The principal chemical loss process for nitric acid is its reaction with ammonia to form ammonium nitrate (NH_4NO_3). This reaction, which is reversible, is believed to be the primary source of fine (<2.5 μm diameter) nitrate aerosol in California's urban air.

Ambient concentrations of secondary particles are not necessarily proportional to the quantities of emissions since the rates at which they form and their gas/particle equilibria may be controlled by factors other than the concentration of the precursor gas. The rate of NO_X oxidation and the branching ratio between inorganic and organic nitrates are known to depend on the specific environmental conditions in addition to reactant concentrations. The partitioning of inorganic nitrate between gaseous nitric acid, ammonium nitrate, and nonvolatile nitrate is known to depend on a number of factors, such as relative humidity, temperature, and ammonia, in a nonlinear manner.

Fine particles typically are comprised of sulfate, nitrate, ammonium, elemental carbon, organic compounds, and a variety of other compounds. Limited studies indicate that there may be changes in the secondary components due to increased oxidants during weekends. Thus, given the contribution of NO_X and VOC to secondary PM formation, it would be useful to know whether the variations by day of week in these precursors are evident in PM data.

3.1.3 PM Related Data Resources

The particulate data used in this study are available from routine particulate matter monitoring program and the California Acid Deposition Monitoring Program (CADMP). With the routine monitoring program, samples of particulate matter 10 microns or less in diameter (PM10) are collected over a 24-hour period using a high volume sampler equipped with a size selective inlet (SSI) or using a dichotomous (Dichot) sampler. Samples are usually collected from midnight to midnight every sixth day. Compositional analysis currently provides measurements of nitrate, sulfate, ammonium, chloride, and potassium for selected sites. The dichotomous sampler, or virtual impactor, uses a low volume PM10 inlet followed by a split in the flow stream that separates particles into two separate fractions: fine particles (PM2.5, i.e., particles with diameters less than 2.5 μm) and coarse particles (those having diameters 2.5-10 μm). The sum of the fine and coarse fractions provides a measure of total PM10 from the Dichot sampler.

Initially, the CADMP sampler (Watson, et. al., 1991) had two units designed for collection of particulate species in two size fractions and for collection of acidic gases. The PM10 unit collected particles less than 10 μm

aerodynamic diameter on a Teflon filter, and had impregnated back filters for collection of ammonia and sulfur dioxide. The Teflon filter was analyzed for sulfate, nitrate, chloride, ammonium, sodium, magnesium, calcium, and potassium ions. The PM2.5 unit collects two samples of particles less than 2.5 µm aerodynamic diameter, one on a Teflon-nylon filter pack without a nitric acid denuder, and the other on a nylon filter after a denuder (consisting of anodized aluminum tubes). The Teflon filter is analyzed for the same species as the PM10 Teflon filter while the nylon back filter is analyzed for nitrate ions. Concentrations of dry-deposition particles and gases were measured by collecting consecutive 12-hour daytime and nighttime samples (day: 0600 to 1800 PST; night: 18:00 to 0600 PST), once every sixth day. In September 1995, the CADMP network was reduced to five monitoring sites in urban areas (Azusa, Bakersfield, Long Beach, Los Angeles, and Sacramento). The sample collection schedule was changed from two 12-hour samples to one 24-hour sample commencing at midnight like the routine particulate matter monitoring network; in addition, the sampling was reduced to PM2.5 monitoring only.

The PM10 Technical Enhancement Program (PTEP) monitoring (Kim, et. al., 2000a) was established at six sites including: downtown Los Angeles, Anaheim, Diamond Bar, Rubidoux, Fontana, and San Nicolas Island. At each location, sampling equipment were deployed to collect fine and coarse particulate fractions for speciation as well as nitric acid, elemental carbon, ammonium and metals. Total mass was determined gravimetrically as collected on Teflon filters, and the concentrations of 36 trace elements were determined by energy dispersive x-ray fluorescence. Quartz fiber filters were used to collect samples to be analyzed for organic carbon and elemental carbon using an optical thermal carbon analyzer. Water-soluble ionic species, such as nitrate, sulfate, ammonium, chloride, and sodium were extracted from the quartz filters and analyzed by ion chromatography. Two gaseous species, nitric acid and ammonia, were determined by the denuder difference method. PTEP sampling was conducted on a one in six-day schedule (except for Rubidoux, which was sampled once every three days) from January to March of 1995. The sampling frequency was increased to once every three days from April to June, and then to every day from July to December 1995 (except for San Nicolas Island which remained on a one in six-day schedule for the entire year). During the second half of 1995, although sampling was scheduled every day except at San Nicolas Island, PM10 and PM2.5 chemical speciation were conducted only every third day. However, PM10 and PM2.5 mass was determined for each daily sample. During the PM episodes, chemical speciation was conducted every day.

Continuous particulate monitoring methods have evolved in recent years. The hourly data from these methods provide additional insight into the nature of the particulate problem and remove uncertainties associated with less than daily sampling frequencies. However, the current designs of these instruments do not permit analysis for ionic and elemental constituents. The

more commonly used continuous PM monitor in California is the tapered element oscillating micro-balance (TEOM). A potential limitation of this monitor is that it is heated to 30 - 50 degrees Celsius to eliminate humidity effects under a broad range of ambient operating conditions. At locations where and times when volatile secondary particles such as nitrates and some organics are a significant portion of the total particulate mass, the PM measurements are obviously lower with the TEOM than with the traditional high-volume sampler with SSI.

At the Sacramento and Azusa sites, data on light scattering (gathered with a nephelometer) and on light absorption (the coefficient of haze) are also available. Coefficient of haze (COH) and light scatter (B_{scat}) provide a relative indication of the contributions of light absorption and light scattering. The COH is a direct measure of the light-absorbing ability of the particles. Light absorption is primarily due to elemental carbon from combustion. The B_{scat} roughly measures all scattering by fine particles. The characteristics of light scattering are extremely sensitive to the size of the scattering particles. Light scattering by the large particles (>10 μm diameter) is generally not significant. As particle sizes approach the range of light wavelengths (0.1-1 μm) they become more efficient in light scattering. COH units are defined as the quantity of particulate matter that produces an optical density of 0.01 on the paper tape. A photometer detects the change in the quantity of light transmitted through the spot as the particulate matter collects on the paper filter tape and produces an electrical signal proportional to the optical density. A COH of less than 1.0 represents relatively clean air while a COH of greater than 2.0 represents air with a relatively high concentration of combustion-generated particles.

From 1989 through 1998, the SSI-PM10 sampling network includes 21 sampling sites in the South Coast Air basin (SoCAB). Of these, Avalon and Los Alamitos had very limited data. Hence, the data from these two sites were not analyzed. SSI-PM10 data were also analyzed for three regions: San Francisco Bay Area (11 sites), Sacramento Valley (14 sites), and San Joaquin Valley (14 sites). SSI-PM10 species used in this study include only nitrate and sulfate ions. In SoCAB, three of the 19 sites have parallel dichotomous samplers: Azusa, North Long Beach, and Riverside-Rubidoux. To assess the comparability of the SSI and Dichot sampling methods, PM10 measurements, matched by site and date, were plotted against each other. Most of the collocated data indicate good agreement between these two sampling methods. The quality of the CADMP data is comparable to that of the other PM2.5 and PM10 samplers and is a valuable source of data that has been largely untapped.

3.1.4 Methodology

The general approach was to first analyze day-of-week patterns of PM10 and PM2.5 concentrations. We performed statistical tests to provide an

indication of the magnitude of the systematic differences between days of the week relative to random day-to-day variation. Where significant differences exist, we would then determine which species contribute to the differences.

Since the ambient air quality standards for PM are based on geometric means, we first calculated the geometric means of SSI-PM10 for each day of the week for each site for the period 1989-1998. The pattern showed Sunday being generally lower than other days of the week. However, to determine statistical significance of the differences between days of the week, we performed a rigorous analyses as follows.

We adjusted for seasonality and trend by taking residuals (differences between actual and fitted values) from a smoothing spline. Splines have an advantage over other smoothing methods when applied to complex data sets in that their degree of smoothness is locally adaptive, rather than being uniform over the range of the data. The degree of smoothness was selected by generalized cross validation to yield a curve which followed the seasonal pattern and trend without excessive roughness. The residuals (observed value minus fitted value) from the spline fit, henceforth referred to as the *adjusted concentrations*, were largely uncorrelated and symmetrically distributed.

Treating the adjusted concentrations for different days of week as independent, we computed group means and standard errors. The assumption of independence is reasonable because PM samples are collected 6 days apart, long compared to the time scale of daily meteorological events which strongly impact atmospheric concentrations.

We compared days of the week by examining error bar charts of adjusted concentration (see attached charts). The width of the error bars was set to a 97.5% confidence interval to yield an approximate 95% confidence level for pairwise comparisons between days. If the error bars for two days do not overlap, the means are significantly different at the 95% level of confidence. Numbers next to the means indicate sample sizes.

To ensure that the seasonal adjustment procedure did not introduce artifacts, we compared results against geometric means. While there were minor differences between the geometric means of the raw and the arithmetic means of the residual concentrations, they do not affect to the overall conclusions.

The above test of significant differences between days of the week was performed for SSI-PM10 at all 19 sites and various PM species at the 3 dichotomous and CADMP sites.

To confirm the statistical results, we used the SAS GLM (general linear model) procedure to perform analysis of variance on day-of-week means,

including fixed effects for month crossed with year. In order to stabilize the error variance and reduce the effect of extreme observations, we transformed the data according to the relationship $y = \log(x)$, rendering the transformed data as normally distributed since the original data is lognormally distributed. We compared the GLM significance levels for pairwise comparisons of days of week against the error bar charts. The GLM tends to report slightly higher significance levels than the charts, which is expected since the confidence bounds used to generate the charts are conservative.

For the 3 dichotomous, SSI, and CADMP sites, we calculated geometric means of PM10, PM2.5 mass and species.

For the 3 dichotomous and CADMP sites, we also calculated geometric means for separate seasons (winter, spring, summer, and fall) and separate time periods (1989-1991, 1992-1994, and 1996-1998), avoiding the introduction of reformulated gasoline regulations in 1995.

For the PTEP data, the means are arithmetic means of quarterly arithmetic means, where the quarters are defined to be: quarter 1 – Jan-Mar; quarter 2 – April-June; quarter 3 – July-September, and quarter 4 – October-December of 1995. Unlike the SSI and Dichot data sets, where the sampling frequency was equal across months, the PTEP data had uneven sample sizes for the months. Hence, we adopted this calculation to better reflect the unequal sample count and mirror US EPA standard calculations of the means of quarterly arithmetic means.

The crustal component of both PM10 and PM25 was calculated by:

$$\text{Crustal} = 2.20*\text{Al} + 2.19*\text{Si} + 1.63*\text{Ca} + 2.42*\text{Fe} + 1.94*\text{Ti}.$$

We have applied the similar statistical methods used for SSI, Dichot and CADMP on the PTEP data (that is, spline smoothing, residuals, then 97.5% confidence bars, etc). The PTEP graphs indicate the confidence intervals for significance testing on the total mass of PM10 and PM2.5. Similar graphs of confidence intervals were also created for the various species of PM10 and PM2.5 (graphs are not presented).

3.1.5 Discussion of Results

The most abundant components of PM10 and PM2.5 in SoCAB are ammonium, nitrate, sulfate, and elemental carbon. Aluminum, silicon, calcium, manganese, and iron are abundant only in coarse PM10. Concentration of crustal components is low at urban areas, where most of the road surfaces are paved. Nitrate is the largest chemical component of both PM10 (23-26% of the PM10 mass) and PM2.5 (28-40% of the PM2.5 mass) in the Basin. The major components of the “others” (unexplained portion of the measured PM mass) in the PTEP database are water and trace metals, and in the CADMP database are organic compounds, water, and trace metals.

Analyses of PM10 mass from the SSI and CADMP samplers show that Sunday is the lowest day of the week at many sites, often significantly different from mid-week. This might be due to lower road dust related to lower car and truck traffic. The Saturday mean concentration is comparable to weekdays but generally slightly lower than Friday. Roughly half of the sites show a slight dip on Wednesday. Some sites show Thursday as being the highest day during the week. Dichot-PM10 (the sum of coarse and fine fractions) tracks the same pattern as SSI-PM10 at Azusa, North Long Beach, and Riverside. The coarse fraction is significantly lower on Sunday and Saturday at Azusa, but not at North Long Beach and Riverside-Rubidoux. Across periods, PM has decreased considerably. Because of the limited amount of data for each season and period, no significance testing was performed on day-of-week differences, and no results are shown.

Significance testing of CADMP data shows PM10-daytime adjusted concentrations being significantly lower on Saturday and Sunday than weekdays at Azusa. For other sites and individual species, results for daytime, nighttime, and 24-hour samples do not show significant day-of-week differences at 95% level.

The results of the SSI-PM10 data at San Francisco Bay Area, San Joaquin Valley, and Sacramento Valley show no “weekend effect” for PM10. Though Sunday shows the lowest PM10, followed by Wednesday, then Saturday, at many sites, the differences are not significant at 95% level. Since there was no significant PM10 effect, we did not need to investigate PM at the individual species level.

Analyses of PM10 mass from the CADMP and TEOM samplers show that Sunday is the lowest day of the week at three sites in SoCAB, often significantly different from mid-week. TEOM-PM10 data do not track the same pattern as the CADMP-PM10 data at Azusa, Downtown LA and North Long Beach. Weekday TEOM-PM10 changes are less pronounced than those using the CADMP-PM10 data. Across periods, day-of-week patterns of TEOM-PM10 are relatively similar for each season and period.

Day-of-week patterns of the TEOM-PM10 data do not track the same pattern as B_{scat} data at all sites. The day-of-week patterns for B_{scat} show no change or a small change. Results of a visibility modeling study (Wexler et al., 1992) indicate that light-scattering particles dominate the visibility problem, and light absorption (mainly by black carbon particles) makes an increasingly important contribution to the extinction coefficient in the fall and winter months. Also, the results of this study show that collocated nephelometers are often in disagreement, and that no visibility model can be expected to produce exact agreement with all measured light scattering values because the light scattering data are in conflict. Please note that during the 1987 Southern California Air Quality Study (SCAQS), the light scattering values were

measured by several investigators using heated or non-heated nephelometers or even slightly different instrumentation for measuring light scattering.

At the Sacramento site, the day-of-week pattern of the TEOM-PM10 data are associated closely with the COH data. Recall that the COH is a direct measure of the light absorbing ability of the particles. Light absorption is primarily due to elemental carbon from combustion. Since elemental carbon accounts for about 10-15% of total fine particle mass in the South Coast Air Basin, reduced emissions of this primary PM component can potentially contribute to reduced ambient PM concentrations and associated reduced light extinction. Traffic count data in the SoCAB show a decrease in heavy-duty vehicle travel on weekends. Since heavy-duty trucks typically represent a major source of black carbon, the decrease in heavy-duty truck travel may also result in a decrease in ambient elemental carbon concentrations, and perhaps a decrease in PM light extinction as well. High concentrations of PM, elemental carbon in particular, may reduce the amount of light energy (photons) available to fuel ozone photochemistry near the surface.

Examination of results at each of the PTEP sites indicates a weekly pattern with the maximum concentrations occurring on Thursday or Friday and the minimum occurring on Saturday or Sunday at all five sites for PM10 mass. PM2.5 concentrations on Wednesday are lower than on the other weekdays at Anaheim and Rubidoux; however, a PM2.5 Wednesday maximum occurs at Los Angeles-North Main and Fontana. Average PM10 and PM2.5 concentrations showed strong spatial variations with low concentrations in coastal areas and high concentrations in inland areas. Analysis of the PM species indicates that ammonium and nitrate show a strong spatial variation with low concentrations at coastal locations and high concentrations at inland locations. This is partly due to transported precursor emissions having more time to react with nitric acid. Sulfate concentrations do not show strong spatial variations. Dichot-PM2.5, SSI-nitrate, and SSI-sulfate are virtually the “same” for all days of week. Although elemental carbon concentrations do not show a strong spatial variation, the Los Angeles-North Main site has the highest elemental carbon concentration because it is in the most dense traffic area in SoCAB.

3.1.6 Conclusion

The formation of secondary particles, which are a major contributor to the fine PM levels in California, from precursors is a complex, nonlinear process, so we should not expect to see a one-to-one relationship between precursor emissions and ambient secondary PM concentrations. For example, there are several factors influencing the relationship between NO_X emissions and particulate nitrate concentrations, which might act to reduce the impact of decreases in weekend NO_X emissions on ambient 24-hour average nitrate concentrations. For example, photochemical conditions that lead to higher ozone on weekends may also increase the fraction of NO_X that is converted to

nitric acid and particulate nitrate. Also, PM measurements summarized in several studies are from 24-hour integrated samples and thus represent the influence of emissions throughout the day. While morning NO_X emissions are reduced on weekends, emissions at other times of the day have not been analyzed and may or may not differ between weekends and weekdays.

In summary, given the wide variety of sources contributing to PM (e.g., primary particles and secondary particles from combustion sources) and the factors listed above, interpretation of these results in terms of weekday/weekend emissions differences is complex and should be done with caution. Performing a comprehensive air quality data analysis and three-dimensional modeling study that would test the impact of emissions changes associated with changes in emission levels, timing, spatial distributions, etc, would lead to a more accurate characterization of the weekday/weekend behavior of PM.

3.1.7 Recommendations

Aside from the observation that morning NO_X levels measured by routine methods (at sites where such data are available) are lower on Saturday and Sunday, in general little is known about weekly patterns in other precursor concentrations (e.g., VOCs). Therefore, NO_X patterns provide only a partial picture of the impact of weekday-weekend emission differences on ambient precursor levels.

The results of the 1997 Southern California Ozone Study (SCOS97) Caltech aircraft sampled aerosols exhibited a complex vertical structure possessing multiple elevated aerosol layers. The overall picture that has been obtained from these airborne observations is of a highly complex aerosol structure which is not consistent with the simple consideration of a mixed layer in contact with the ground that is trapped below a temperature inversion. Additional measurements are necessary to determine whether the presence of these strong gradients follows a diurnal pattern.

The impact of meteorological variables on PM mass and its components needs to be evaluated. Weather plays a big role in what primary particles are emitted, and to what degree. Secondary pollutant formation is influenced by a combination of precursor pollutant concentrations and weather conditions. Conversion of SO_X to sulfate aerosols is accelerated by the presence of oxidants and OH radicals in the air (as during ozone episodes) and is accelerated even more under humid conditions when the conversion can occur inside water droplets. NO_X conversion to nitrate is even more sensitive, as formation rates must compete with dissociation back to gases, so that nitrate is generally a cool-wet (e.g., winter) phenomenon.

Finally, performing a comprehensive 3-D modeling study that would test the impact of emissions changes associated with changes in emission levels,

timing, spatial distributions, etc., would permit hypothesis testing with the most comprehensive tools available.

3.1.8 References

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